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(54) Process for the preparation of hydrocarbons

(57) Process for the catalytic preparation of hydrocarbons containing at least two carbon atoms per molecule from a gas mixture comprising hydrogen and carbon monoxide, which comprises passing the gas mixture through a reaction zone containing catalyst particles, while removing heat from the reaction zone by a cooling medium which flows via one or more helical patterns, each pattern containing one or more helices.

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## PROCESS FOR THE PREPARATION OF HYDROCARBONS

The invention relates to a process for the catalytic preparation of hydrocarbons containing at least two carbon atoms per molecule from a gas mixture comprising hydrogen and carbon monoxide by passing the gas mixture through a reaction zone containing catalyst particles.

Processes for the conversion of synthesis gas (i.e. a gas mixture comprising hydrogen and carbon monoxide) into hydrocarbons are known. As such conversions are highly exothermic processes, it will be appreciated that usually means have to be used for the removal of heat from the reaction zone. For instance, a suitable reactor is a multitube reactor in which a cooling medium flows through the spaces between the tubes. The tubes are filled with suitable catalyst particles. Synthesis gas flows in downward direction through the tubes, and the reaction products are removed from the bottompart of the reactor.

Nowadays there is an increasing demand for larger capacity equipment, not only because all (chemical) processes are carried out on ever larger scale but also because certain processes are increasingly used. In particular the synthesis of hydrocarbons containing at least two carbon atoms per molecule by conversion of carbon monoxide and hydrogen, prepared for instance by gasification of coal, attract increasing interest.

Upscaling of a reactor of the above multitube type to increase the capacity thereof may, however, have a severe adverse influence on the efficiency, particularly if the reactor is used for carrying out highly exothermic reactions, such as the conversion of carbon monoxide and hydrogen into hydrocarbons. In this highly exothermic reaction the heat liberated has to be removed continuously to avoid undesirably high temperatures which might cause a sharp increase of the rate of reaction (possibly followed by deactivation of the

catalyst) and/or the occurrence of unwanted side reactions. The aim of continuous heat removal, in exothermic reactions means with respect to tube type reactors that the tubes forming the reaction zones must have a relatively small cross-sectional area with a heat transfer medium circulated around the outer surfaces of the tubes. If the cross-sectional areas of the reaction zones are large, the middle parts of the zones are too far away from the heat transfer medium at the outside of said zones and hence tend to experience undesirable temperature increases or temperature drops. Increase of the capacity of a tube type reactor should therefore be accomplished by an increase of the number of tubes rather than by an increase of the tube diameters. The use of a large number of tubes enclosed in a necessarily large diameter reactor vessel poses, however, a number of problems, viz. firstly it becomes difficult to achieve uniform distribution of heat transfer medium over the full diameter of the reactor vessel, secondly uniform distribution of fluids over the various tubes becomes more difficult. A uniform distribution of heat transfer medium along the tubes is required to obtain a reaction product with a predetermined constituency and to prevent stresses in the bundles of tubes due to temperature differences.

An object of the present invention is to overcome the above problems encountered with increasing the capacity of tube type reactors suitable for carrying out highly exothermic reaction as the catalytic preparation of hydrocarbons from hydrogen and carbon monoxide.

It has now been found that the catalytic preparation of hydrocarbons containing at least two carbon atoms per molecule very suitably may be carried out in a reactor comprising a catalyst bed wherein one or more helical wound cooling tubes have been installed, the reactor being maintained at conversion conditions.

The use of this type of reactor does not lead to the problem encountered with the increase of the capacity of a multitube reactor, especially the uniform distribution of heat transfer medium over the full diameter of the reaction vessel and along the tubes. Also a higher heat transfer of the process side is obtained,

and no use has to be made of very large diameter tube sheets. Another advantage is that the thickness of the wall of the reactor is determined by the process pressure and not by the pressure of the cooling medium, as the process pressure is usually lower than the pressure of the cooling medium. The helical wound cooling tubes does not give large expansion problems, which makes the reactor less sensitive to temperature differences between the tubes and the reactor wall. Further, catalyst loading and unloading is easier in this type of reactor than it is in a multitube reactor.

10       The process of the present invention, therefore, relates to the catalytic preparation of hydrocarbons containing at least two carbon atoms per molecule from a gas mixture comprising hydrogen and carbon monoxide, which comprises passing the gas mixture through a reaction zone containing catalyst particles, while  
15       removing heat from the reaction zone by a cooling medium which flows via one or more helical patterns, each pattern containing one or more helices.

      To obtain the helical patterns of the cooling medium helical wound tubes or tube bundles are used. Preferably a cylindrical  
20       reaction vessel is used provided with one or more helical wound tubes or tube bundles, each tube bundle comprising two or more helical wound tubes of substantially the same dimensions, and situated in a concentric ring or a number of concentric rings around the central axis of the reaction vessel. Thus, the cooling  
25       medium flows via one or more helical patterns situated concentrically around the central axis, each pattern containing one or more helices. When two or more concentric tubes or tube bundles are used, the screw-direction of the helices of two adjacent tubes or tube bundles are preferably opposite to each other. When two or  
30       more tube bundles are used it is preferred to use an increasing number of helical wound tubes in bundles situated at a larger distance from the central tube, and to maintain substantially the same length for each tube.

      The helical flowing pattern of the cooling medium enables the  
35       ratio heat-exchanger surface/reactor volume to be varied over a

large range. The tube diameter may be varied as well as the distance between two layers of tubing in both the axial and the radial direction. The diameter of the cooling tubes is suitably chosen between 4 and 55 mm, especially between 10 and 35 mm. The distance  
5 between two adjacent rings of tubes or tube bundles (distance in the radial direction) is suitably chosen between 10 and 50 mm, especially between 15 and 25 mm, and the distance between two adjacent coils lying in a concentric ring (distance in the axial  
10 direction) is suitably chosen between 10 and 200 mm, especially between 10 and 50 mm. The helical wound tube bundles make it possible to use hemispheric tube sheet designs, thus avoiding the less suitable flat tube sheets.

The heat exchange tubes are preferably spaced in such a manner in the reaction zone(s) that an optimal temperature profile is  
15 attained therein in radial direction. Moreover, each group (e.g. concentric ring) of heat exchange tubes may be in communication with separate cooling fluid in- and outlet means which can be operated independently of other groups of heat exchange tubes in order to attain optimal control over the temperature profile in the  
20 reaction zone(s).

Water is usually used as cooling medium. Preferably the water evaporates at least partially in the tubes. This enables the heat of reaction to be removed from the reaction zone by producing steam. Other cooling media as organic compounds, for instance  
25 biphenyl, thermal oils or liquid metals may also be used.

The process according to the invention is particularly suitable for converting a synthesis gas feed (at least partly) into hydrocarbons having at least 5 carbon atoms per molecule, preferably having at least 10 carbon atoms per molecule; most preferably  
30 paraffinic hydrocarbons having at least 20 carbon atoms per molecule are prepared. It is remarked that when a substantial part of the hydrocarbons contain 20 carbon atoms per molecule (which will be the case when the major part of the hydrocarbon molecules contain at least 10 carbon atoms per molecule) a considerable part  
35 of the reaction product is a liquid under the usual conditions

maintained during the reaction. Especially when a (partly) liquid product is obtained problems could have been expected due to liquid uphold and the occurrence of flow patterns. In case of a reaction product containing an average of 10 carbon atoms, most of the  
5 reaction products will be gaseous under the usual reaction conditions and only a small amount of liquid product will be formed.

The synthesis gas feed referred to hereinabove contains as major components hydrogen and carbon monoxide; in addition said feed may contain carbon dioxide, water, nitrogen, argon and minor  
10 amounts of compounds having 1-4 carbon atoms per molecule such as methane, methanol or ethene.

The synthesis gas feed can be prepared in any manner known in the art e.g. by means of steam/oxygen gasification of a hydrocarbonaceous material such as brown coal, anthracite, coke, crude  
15 mineral oil and fractions thereof, and oil recovered from tar sand and bituminous shale. Alternatively, steam methane reforming and/or catalytic partial oxidation of a hydrocarbonaceous material with an oxygen-containing gas can be applied to produce synthesis gas excellently suitable for use in the process according to the  
20 invention.

The present process is preferably carried out at a temperature from 100-500 °C, a total pressure from 1-200 bar abs. and a space velocity from 200-20,000 m<sup>3</sup> (S.T.P.) gaseous feed/m<sup>3</sup> reaction zone/hour. Particularly preferred process conditions for the  
25 preparation of hydrocarbons include a temperature from 150-300 °C, a pressure from 5-100 bar abs. and a space velocity from 500-5000 m<sup>3</sup> (S.T.P.) gaseous feed/m<sup>3</sup> reaction zone/hour. The expression "S.T.P." as referred to hereinbefore means Standard Temperature (of 0 °C) and Pressure (1 bar abs.). In case synthesis  
30 gas is employed as gaseous feed, the H<sub>2</sub>/CO molar ratio therein is preferably from 0.4-4 and most preferably from 0.8-2.5.

Suitable catalysts for the preparation of (paraffinic) hydrocarbons from synthesis gas contain at least a metal (compound) from Group 8 of the Periodic Table of the Elements, preferably a non-  
35 noble metal, in particular cobalt, optionally in combination with a

noble metal e.g. ruthenium, on a refractory oxide carrier such as silica, alumina or silica-alumina, in particular silica or alumina. Furthermore, the catalysts preferably contain at least one other metal (compound) from Group 4b and/or 6b, most preferably chosen from the group consisting of zirconium, titanium and chromium. The catalysts preferably contain from 3-60 parts by weight of cobalt, optionally 0.05-0.5 parts by weight of ruthenium, and from 0.1-100 parts by weight of other metal(s) per 100 parts by weight of carrier.

10       The metals may be incorporated into the catalyst by means of any method known therefor in the art, such as (gas)impregnation (e.g. in the form of chlorides or carbonyls), ion-exchange, kneading or precipitation. Kneading and impregnation are preferred methods, the latter in particular for the incorporation of cobalt.

15       The resulting catalyst composition is preferably calcined at temperatures from 350-700 °C after each impregnation or kneading step.

20       The catalysts are preferably employed in the present process in the form of spherical, cylindrical or lobed particles with a diameter from 0.1-15 mm, and in particular from 0.5-5 mm. The catalyst carrier particles can be prepared by means of any method known in the art, such as pressing or extruding of powdery catalyst material, if desired together with a binder material. Catalyst carrier spheres, in particular silica-containing spheres, are

25       suitably prepared by means of the "oil-drop" method whereby said spheres are formed as drops of a silica gel which are solidified while falling in an oil bath. Alumina based carriers are preferably made by extrusion.

30       The catalyst present in the reaction zone(s) may be kept in contact with liquid product in case relatively heavy paraffins (with more than 20 carbon atoms per molecule) are synthesized with the present process in order to avoid the formation of carbonaceous deposits on the catalysts. Liquid redistribution means (e.g. in the form of trays or layers of material having a relatively low permeability for liquid and/or gas) can be arranged above the reaction

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zone(s) in order to promote substantially the equal distribution over the catalyst bed and the desired optimal contact with liquid product.

5 Furthermore, the invention relates to liquid products whenever prepared by a process as described hereinbefore.

10 In addition, the invention relates to an apparatus whenever used for carrying out the process as described hereinbefore which apparatus comprises a housing having gaseous feed inlet means and product outlet means and enclosing at least one reaction section which is in communication with the feed inlet means and via collection means with the product outlet means, which collection means are arranged relative to the reaction section(s) such that a substantially radial flow pattern can be maintained in said section(s).



C L A I M S

1. Process for the catalytic preparation of hydrocarbons containing at least two carbon atoms per molecule from a gas mixture comprising hydrogen and carbon monoxide, which comprises passing the gas mixture through a reaction zone containing catalyst particles, while removing heat from the reaction zone by a cooling medium which flows via one or more helical patterns, each pattern containing one or more helices.
2. Process according to claim 1, wherein the cooling medium flows through two or more concentric helical patterns.
3. Process according to claim 2, wherein the screw direction of adjacent helical patterns are opposite to each other.
4. Process according to claim 2 or 3, wherein an increasing number of helices is used in the helical patterns which are situated at a larger distance from the centre.
5. Process according to claim 4, wherein the helices have substantially the same length.
6. Process according to any one of the preceding claims wherein a synthesis gas feed is converted into hydrocarbons having at least 5 carbon atoms per molecule, preferably having at least 10 carbon atoms per molecule.
7. Process according to any one of the preceding claims which is carried out at a temperature from 100-500 °C, a total pressure from 1-200 bar abs. and a space velocity from 200-20,000 m<sup>3</sup> (S.T.P.) gaseous feed/m<sup>3</sup> reaction zone/hour.
8. Process according to any one of the preceding claims in which a catalyst is used comprising 3-60 pbw cobalt and 0.1-100 pbw of at least one other metal chosen from the group formed by zirconium, titanium and chromium per 100 pbw of silica, alumina or silica-alumina carrier.
9. Process for the catalytic preparation of hydrocarbons according to claim 1, substantially as described hereinbefore.

10. Hydrocarbons whenever prepared according to a process as claimed in any one of the preceding claims.

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